X-ray absorption fine structure measurement with a 9 V electric battery x-ray emitter

Mitsuya, S; Ishii, H; Kawai, J; Tanaka, K

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X-ray absorption fine structure measurement with a 9 V electric battery x-ray emitter

Shota Mitsuya, Hideshi Ishii, and Jun Kawai[a)]
Department of Materials Science and Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

Keiichi Tanaka
SII NanoTechnology Inc., 563 Takatsuka-Shinden, Matsudo 270-2222, Japan

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X-ray absorption spectral analysis is a well known technique for analyzing the chemical environment of an element in a specimen. It has been believed that high intensity and monochromatized x rays such as the synchrotron radiation are required for an x-ray absorption experiment. In the present study, however, we demonstrate that the x-ray absorption spectral measurement of transition metal foils with an energy resolution of 10 eV is possible with a combination of a 9 V dry electric battery pyroelectric x-ray generator and a superconducting microcalorimeter. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2356462]

It has recently been believed that monochromatized high intensity synchrotron radiation x rays are required for x-ray absorption spectroscopy, though low power x-ray tubes were used at an early age of the x-ray absorption spectroscopy. Miniature x-ray sources using a charging phenomenon of an insulator have been reported by several authors.[1–4] Recently, a small x-ray emitting device using the pyroelectric charging effect has become commercially available. This device emits x rays driven only by a 9 V dry electric battery. Ida and Kawai[5] reported the x-ray fluorescence (XRF) quantitative analysis of a small amount of Cr (0.09 wt %) in steel, demonstrating the capability of the x-ray emitter as a source for a portable XRF instrument. Recently Ishii and Kawai[6] reported an x-ray absorption spectral measurement of Ca in paper using the pyroelectric x-ray device and a Si *p-i-n* type detector. Although the Ca *K* edge was observable, the energy resolution was insufficient due to the low energy resolution of the x-ray detector (200 eV at 5.9 keV). In the present study, we report the *K*-edge x-ray absorption spectral measurement of Ti and Co foils using the dry electric battery x-ray generator and a microcalorimeter using the superconducting transition edge, which has a higher energy resolution (10 eV) than a Si *p-i-n* detector.

The x-ray emitter used in the present measurements was a COOL-X (Amptek, Beford, MA). This x-ray emitter was cylindrical shaped with a 14 mm diameter and a 10 mm height. The pyroelectric crystal in the COOL-X was $LiTaO_3$, and the target metal was Cu. X rays were generated by the collision of electrons with the pyroelectric crystal as well as the Cu-metal target due to the electric polarization of the crystal. When the temperature of the crystal is changed by heating and cooling the crystal by a Peltier device, the existing polarization was increased (below the Curie temperature the pyroelectric crystals are spontaneously polarized). Because the electric power applied to the Peltier heater/cooler was less than 300 mW, the COOL-X can emit the x rays which are consisted of Cu *K* and Ta *L* lines as well as the bremsstrahlung driven only by a 9 V 006P battery.

The x-ray detectors used in the present study were either a Si *p-i-n* detector (Amptek) or a microcalorimeter using the superconducting transition edge (SII NanoTechnology, Tokyo, Japan).[7,8] The microcalorimeter had a high energy resolution (14 eV at 1.5 keV), which consisted of a thermometer using the superconducting transition edge, an x-ray absorber, and the thermal link. The operation point was kept within the superconducting transition temperature by the balance between the Joule heating and the heat through the thermal link from the thermometer to the thermal bath.

X-ray absorption of thin foil of thickness d is expressed by the relation $I=I_0\exp(-\mu\rho d)$, where μ and ρ are the mass absorption coefficient and mass density, respectively. According to this expression, the x-ray absorption spectra can be obtained by dividing the x-ray intensity before the transmission of a thin foil (I_0) by the x-ray intensity after the transmission (I). In order to obtain the x-ray absorption spectra, both the direct incident and the transmitted x-ray spectra should be measured.

Because the COOL-X emits white x rays ranging mostly from 4 to 9 keV, thin foils which have the absorption edges in this energy range were appropriate for the measurement. Using a too thick foil, the intensity of the transmitted x rays became too weak; using a too thin foil, the jump of the absorption edge became small. The ideal thickness of the foil was estimated to be several micrometers, and consequently Ti foil of 2 μm and Co of 4 μm were measured.

The experimental geometry is shown in Fig. 1. All of the measurements were carried out in air. The thin foil was placed perpendicular to the x-ray optical axis as $\theta=90°$, as shown in Fig. 1. In order to change the effective thickness, the spectra were measured with different θ, and the spectra shown in the present letter are those measured at $\theta=90°$.

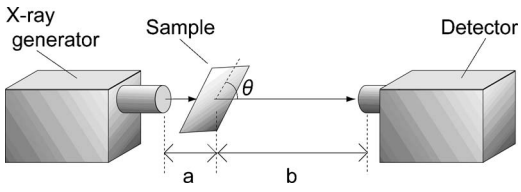

FIG. 1. Experimental geometry for x-ray absorption spectral measurement.

[a)]Electronic mail: jun.kawai@materials.mbox.media.kyoto-u.ac.jp

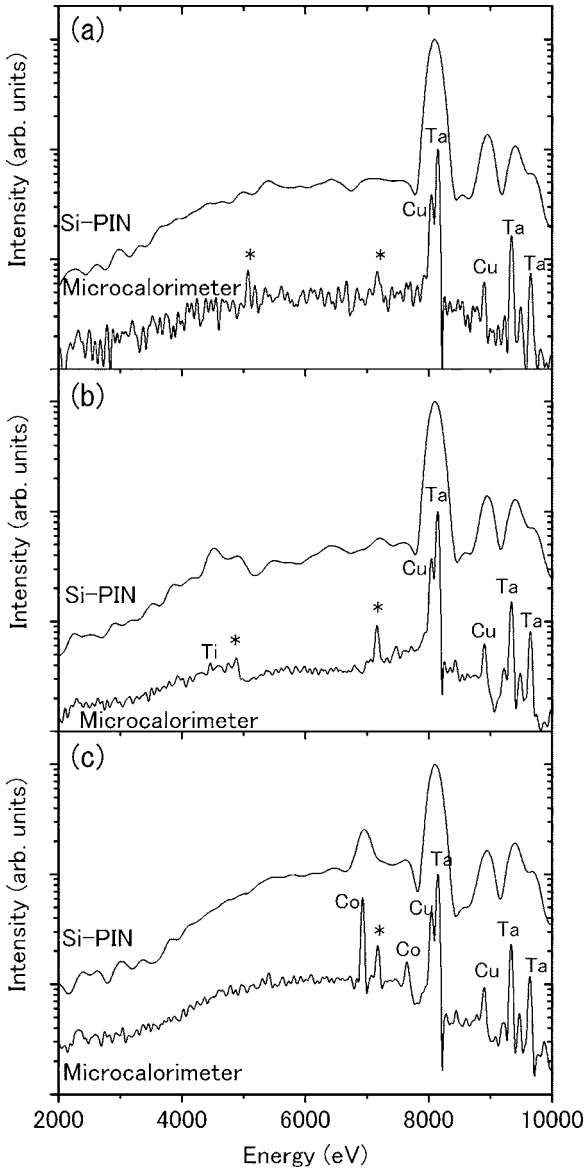

FIG. 2. Representative measured x-ray spectra of (a) direct, (b) Ti transmission, and (c) Co transmission. Peaks denoted by an asterisk were due to noise.

Because the foil emitted fluorescent x rays, the thin foil was placed apart from the detector, as $a \ll b$ in Fig. 1, to avoid detecting the x-ray fluorescence. The Si *p-i-n* detector was placed at 12 cm from the x-ray emitter; the thin foil was placed at 2 cm from the x-ray emitter ($a=2$ cm, $b=10$ cm). The duration to measure the direct and transmitted x-ray spectra was 300 s each for the Si *p-i-n* detector, and 20, 180, or 120 min for the microcalorimeter, which was placed at 2 cm from the x-ray emitter, with the thin foil touched to the x-ray emitter window ($a=0$ cm, $b=2$ cm). The measured spectra were numerically smoothed 30 times by the least squares method of Savitzky and Golay (the second order, 25 points).[9]

Figure 2(a) shows the direct x-ray spectra measured by a Si *p-i-n* detector (one channel was 7.3 eV) and by a microcalorimeter (one channel was 2.0 eV), without the metal foil. The spectra were normalized with respect to the maximum of the spectra. The total counts of the raw spectra obtained by a Si *p-i-n* detector and by a microcalorimeter were ca. 44 000 and 8000 counts, respectively. The main peaks were Cu K

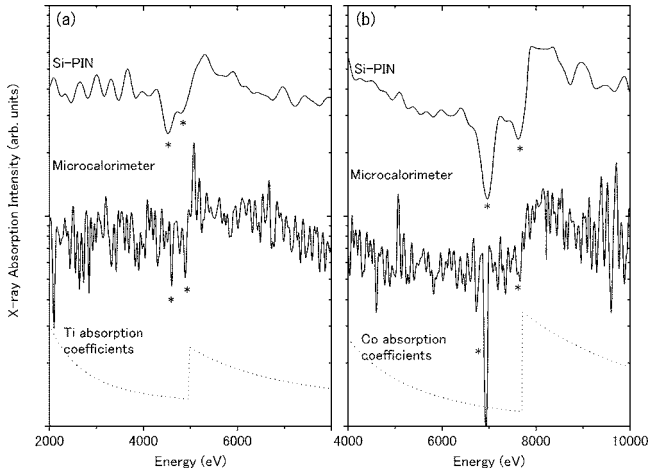

FIG. 3. X-ray absorption spectra of (a) Ti and (b) Co obtained from Fig. 2. The dotted spectra are the plot of mass absorption coefficient taken from Henke *et al.* (Ref. 10). Glitches denoted by an asterisk were due to the x-ray fluorescence from the thin foil. The spectra have been shifted vertically, and the absolute value of the jumping ratios is the same among Si *p-i-n*, microcalorimeter, and value of Henke *et al.* within the experimental error.

and Ta L characteristic x rays from the x-ray generator. Cu $K\alpha$ and Ta $L\alpha$ peaks were clearly separated in the spectrum obtained by a microcalorimeter, although they were not separated by a Si *p-i-n* detector. The origin of the weak peaks at 7200 and 5100 eV detected by a microcalorimeter was due to an electric noise. The spectral intensity below 3500 eV was weak because of the attenuation by the air. Figures 2(b) and 2(c) show the transmission spectra of Ti and Co foils, respectively. The total counts of the raw spectra of Ti foil obtained by the Si *p-i-n* and the microcalorimeter were ca. 36 000 and 77 000 counts, respectively; those of Co foil were ca. 34 000 and 37 000 counts, respectively. All the characteristic x-ray peaks of the microcalorimeter become sharper than that of the Si *p-i-n*.

An x-ray absorption spectrum is obtained by dividing a direct incident x-ray spectrum by the transmitted x-ray spectrum. The absorption spectra obtained in such a way are shown in Figs. 3(a) and 3(b), where I_0/I are plotted in a logarithmic scale. The spectra were normalized with respect to the maximum. The Ti and Co absorption coefficients tabulated by Henke *et al.*[10] are also plotted in Fig. 3.

Although a lot of fine glitches are observed in the spectra, these are within a statistical error. The absorption edges of Ti and Co are distinguishable from glitches. The measured two spectra in Fig. 3(a) have an edge at 5000 eV assigned to the Ti K edge (4964 eV); the measured two spectra in Fig. 3(b) have an edge at 7700 eV due to the Co K edge (7709 eV). Large glitches denoted by asterisks in Fig. 3 near the absorption edges were due to the x-ray fluorescence emitted from the thin foils. Because of the low energy resolution (200 eV) of the Si *p-i-n*, the plotted Ti and Co K edges in the absorption spectra are broad. This is due to the interference with the $K\beta$ fluorescence. However, the Ti and Co K edges of the microcalorimeter were sharper than those of the Si *p-i-n*. Absorption edges were clearly observed with an energy resolution of about 10 eV by using a 9 V dry electric battery x-ray emitter with a superconducting transition-edge sensor x-ray microcalorimeter.

The present result shows that a 9 V battery-powered pyroelectric x-ray generator can be used for x-ray absorption

fine structure spectroscopy when using a high resolution x-ray detector such as a microcalorimeter, and also for clear observation of x-ray absorption fine structure and rapid measurement.

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